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13. ABSTRACT (Maximum 200 words) The rates of gas phase reactions between boranes (B ₂ H ₆ ; B ₅ H ₉ ; B ₁₀ H ₁₄) and oxygen atoms (³ P state) were studied (~350K) in a flow-tube reactor by determining time dependent levels of OH species, as functions of reactant concentrations. Quantitative fitting of these data for B ₂ H ₆ and B ₅ H ₉ led to mechanisms, and estimated rate constants, for the direct attack on the boranes, and for reactions of O(³ P) with fragmentation products (in particular, HBO and HBOH). A degradation sequence was established for each. Measurements (via LIF) of [OH] from B ₁₀ H ₁₄ were not completed; our data show that under comparable conditions the deca produces ~60 fold higher [OH] than does penta. Our QPMS diagnostic of a newly designed flow-tube system and revitalized mass-spectrometer permitted evaluation of a rate constant for the net destruction of B ₅ H ₉ , and qualitative estimates of relative concentrations of B ₅ H ₉ fragmentation products.					
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STATEMENT OF THE PROBLEM:

A). To develop general mechanisms for the reactions of the more stable boranes with atomic $O(^3P)$, at ambient temperatures.

B). To measure quantitatively time dependent OH concentrations, via laser induced fluorescence, generated as the dominant product species, rather than measure overall rates of degradation of the fuels.

C). To develop fragmentation patterns and estimate rate constants for the dominant reactions in the multi-step mechanisms, comparable to those available for the combustion of low molecular weight hydrocarbons.

D). To develop a reliable QPMS diagnostic for the effluents from a well designed flow-reactor, for quantitative assaying of reaction intermediates, generated during the combustion process.

SUMMARY OF RESULTS:

a) A low pressure (5 - 20 Torr) flow reactor was set up; it provides controlled flow rates of measured levels of oxygen atoms, the fuels of interest, and inert carrier gases.

b) A Nd/YAG/Dye laser system was set up for generating pulses of 307.93 nm radiation, to excite a Q-branch line of the ground state of OH to the A state, from which fluorescence is emitted.

c) Fluorescence radiation detection (photomultiplier with filter) digitizing, recording and data processing system was assembled. The photube signal is sent to a BIOMATION 8200, a dual channel Tracor-Northern, and on to a computer for data analysis and plotting.

d) Appropriate thermochemical and kinetic codes were assembled. The available codes for integrating multiple sets of coupled rate equations were extended and tested.

e) Numerous preliminary experiments were run with selected hydrocarbons. C_2H_6 was chosen as a standard for calibrating the output signals, so that the fluorescence intensities recorded for the B/H species could be placed on a quantitative basis, (in mole/liter of OH), that appeared at the sampling pin-hole, centrally located in the flow-tube, and on to the intersection point of the jet with the laser beam. Reaction times were calculated from measured flow rates and location of the fuel injector.

f) A self-consistent, quantitatively scalable mechanism was developed for oxygen atom attack on ethane.

g) A similar mechanism was developed for diborane.

h) A similar mechanism was developed for pentaborane(9); it

i) Rates of OH production in the reactions of $O(^3P)$ with H3BCO and B10H14 were recorded for limited combinations of fuel concentrations and temperatures. These are insufficient for postulating break-down sequences. However, under comparable conditions, B10H14 produces ≈ 60 fold higher levels of OH than does B5H9. Steady-state [OH] is attained in B10H14 at 18 ms post-mixing, whereas steady-state with B5H9 appears at 4 ms.

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